Tar Acid Extraction in a Rotating Disc Contactor

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The extraction of coal tar acids from tar acid oils by means of caustic solutions was investigated in a 4 in. I.D. Rotating Disc Contactor extraction column. This investigation was one phase of a program directed towards the modernization of the coal tar processing plant at Pittsburgh Coke and Chemical Co. Subsequent changes in the economic picture for coal tar derivatives led to a cancellation of the projected modernization.

Two feed stocks from independent manufacturing sources each containing 14-16 wt.% tar acids in neutral oil were employed in the test series. The extracting solution was fresh 9 wt.% caustic in water. These represented the projected plant operating conditions near capacity operation. The tar acid in neutral oil system is chemically indeterminate. Tar acid is a generic name for a mixture of phenol, cresols, xylenols etc. Neutral oil is a mixture of methyl naphthalene, naphthalene, alkyl benzene etc. The acid-oil ratio and the individual constituent ratios are functions of the coal and the coking conditions. Wide variations were normally encountered using local feed stocks which variations were expected to be compounded when outside sources were employed as capacity operation was approached. The 14-16% acid content represented the maximum likely to be encountered over any extended period.

The study also covered the benzene-acetone-water system in order to provide a reference base for the column performance.

The performances of the RDC column are reported for both ternary systems. Certain aspects of the results must be viewed with caution. The measured relative changes in column performance with changes in the levels of the operating variables are believed to be accurate. However, uncertainties with respect to the tar acid equilibrium phase data and its interpretation coupled with the proximity of the operating line to the equilibrium line in these studies make the absolute values of the transfer stage height for this system rather doubtful.

Ternary phase equilibrium data have been published for the benzene-acetone-water system[1]. No data concerning the tar acid oil-aqueous caustic system have been published. The detailed development of the ternary phase diagram for the tar acid oil-caustic system is not reported in this paper. However, some discussion of the approach and the results is essential to the evaluation of the results of the column tests.

Experimental

Absolute analytical techniques for both the tar acid content of, and the species distribution in the feed stock, have not been developed to the point where they are practical on a semi-routine basis. An infrared technique for measuring the

(1) Briggs, Comings, Ind. Engr. Chem. 35, 411 (1943).

concentration of the OH groups was developed which is believed to be fairly reliable[2]. The total weight of acid is then calculated by using an arbitrary molecular weight which agrees with long term plant experience.

Tar acids in the caustic phase were determined by potentiometric titration with HCl to a pH of 8 in alcoholic solution.

The phase boundaries in part and the tie lines were obtained by mixing known weights of tar acid oil and 9 wt.% caustic and analysing the phases for acid distribution. The phase boundaries for a number of feed stocks obtained over a two month period were determined by cloud point titrations according to the method of Othmer[3]. The phase boundary locations for some four feed stocks and a synthetic feed of phenol in naphthalene were very similar over the temperature range between 80° and 95°C. Tie line data scatter rather badly. No positive trend in slope or location as a result of composition or temperature differences could be seen. These data suggest that normal in-plant variations of feed composition should not affect the extraction column performance significantly. A generalized phase diagram was synthesized from all these data.

The column tests were carried out at a later date using two feed stocks which were not a part of the above study. However, the generalized diagram was assumed to apply to the new feeds. This approximation is reasonable in view of the similarity of phenol and cresols with respect to their reactions with caustic. This approximation may not be safe if the concentration of the caustic changed appreciably.

The basic unit of the Rotating Disc Contactor is a cylindrical cell baffled at each end and stirred by a centrally located solid disc. The cells of the pilot column had the following dimensions:

ID	4 in.
Height	2 in.
End baffles	4 in. OD, 3 in. ID, 1/8 in. thick
Rotating disc	2 1/4 in. D, 1/4 in. thick

The early benzene-acetone-water studies and the tar acid extraction studies were carried out in a glass walled column containing 24 cells. The later benzene-acetone-water studies were executed in a stainless steel column containing 36 cells.

Feed and effluent rates were controlled by rotameters. The effluent rates for the tar acid studies are based on continuous weight measurement. The solids precipitated during the acid extraction quickly rendered the rotameters nearly opaque and may have caused some sticking. As a result the use of weigh tanks was adopted.

The interface was sensed and controlled by means of capacitance probes. Solids deposition on the probes during the tar acid extraction forced some modification to the detector system. Two side mounted sight glass chambers were installed with the probe wires wrapped around the outside of the glass at the desired level. Alternate cleaning of the inside of the glasses every 20-30 minutes was found to be satisfactory. After the completion of the column studies a flow system interface detector was developed which was not subject to the problems associated with solids deposition.

The column and auxiliary equipment were steam traced throughout.

(2) Kranc, M.F., Kadavy, D.J., Fassinger, H.M., Paper presented at A.C.S. National Meeting, New York, Sept. 8-13, 1957.
(3) Othmer, D. F. et al, Ind. Engr. Chem. 33, 1240 (1941).

Discussion

The initial dispersion of the phases is generally achieved with the aid of a mixing nozzle. The intensity of interfacial turbulence is probably a maximum at this point. The mean droplet size may be a minimum. The excess mechanically induced turbulence dies out very rapidly and constant relative velocities are approached within a few inches up the column. Where only a few transfer units are attainable in the extraction column a significant fraction of the transfer can occur over this stage. Coalescence of the droplets begins almost immediately after leaving the nozzle.

Performance of the mixing system is one reason why a decrease in the height of a transfer stage is obtained with increasing total throughput when the number of total stages involved is small.

The coefficients of heat or mass transfer per unit area of interface have been shown to depend primarily on the settling rate of the droplets[4]. In stirred systems of this nature the accelerations imposed by the stirrer are a small fraction of that due to gravity. The rate of the stirrer in an RDC column or packing in a packed tower, is therefore the maintenance of a minimum droplet size spectrum. Stirring breaks down the droplets to a size spectrum which appears to depend on the power input per unit volume[5]. The coefficient of mass transfer per unit area falls off at a slower rate than the surface area increases with increasing stirrer speed[4]. That is, the quantity transferred across the interface per unit volume of stirred vessel increases with stirrer speed.

The importance of internal mixing within, and new surface generation on, the droplets as a result of coalescence and breakdown has not been resolved.

In many two phase systems, mixing of the phases at conditions other than equilibrium results in spontaneous interfacial turbulence. Spontaneous emulsification has been observed in a few systems. Random concentration fluctuations along the interface produce viscosity, density, and surface tension gradients. The surface expands and contracts locally. This movement couples with gravity induced convection currents due to density gradients to produce convection cells at the interface[6,7].

Spontaneous interfacial turbulence could be detected under certain conditions with both of the systems under study. The acetone-benzene-water system exhibited turbulence only when the conditions were such that the local solution density could be greater than the liquor density below it. Whether this restriction applies to the phenol in naphthalene-caustic system is not certain. The cell sizes appeared to lie between 0.03 and 0.1 in. diameter.

The mean drop size observed with the benzene-acetone-water system in the RDC column was not more than 3 times the size of the cells observed above at flat interfaces. At such low drop size to convection cell size ratios, development of these convection cells might not be possible.

The presence of surface active agents at the interface does not inhibit normal molecular diffusion. The intrinsic mass transfer coefficient involves both

(4) Calderbank, P.H., Moo-Young, M.B., Chem. Engr. Sci. 16, 34 (1961).
(5) Reman, G.H., Olney, R.B., Chem. Engr. Prog. 51, 141 (1955).
(6) Sterling, C.V., Scriven, L.E., A. I. Ch. E. Journal 5, 514 (1959).
(7) Orell, A., Westwater, J. W., Chem. Engr. Sci. 16, 137 (1961).

turbulent and molecular diffusion. This coefficient has been found to be reduced by the subclass of surface active agents which rigidize the interface[4,8].

Not generally realized is the ability of traces of solids to rigidize an interface. Distilled water exposed to the atmosphere for a few minutes develops a marked surface rigidity as a result of dust deposition[9]. One of the authors has noted the same phenomena with a number of organic compounds.

The benzene-acetone-water system is believed to be free of surface active agents and should be free of solids. However, the extent of the formation of solid precipitates at the interface during extraction of tar acids is such that major reductions in the mass transfer coefficient could have occurred.

The experimental values of the transfer stage height are shown on Figure 1 and 3 for the benzene-acetone-water system and on Figures 2 and 4 for the tar acid in oil-caustic system.

The only significant process variable appears to be the rotor speed both for the benzene-acetone-water and the tar acid in oil-caustic system. For the first system neither the direction of transfer of the acetone, the phase which was dispersed, nor the throughput had significant effects on the number of transfer stages. The flooding point did however depend on the phase which was dispersed, Figure 5. The same pattern was observed with the tar acid in oil-caustic system over the limited ranges studied.

These data suggest that such phenomena as interfacial turbulence, surface rigidity induced by solids accumulation at the interface, and the direction of mass transfer are not normally important variables. The volumetric mass transfer coefficient appears to depend primarily on the droplet size spectrum attainable in the system. However, capacity does depend on the particular phase which is dispersed.

The reader is again cautioned against using the HTS values obtained for the tar acid in oil-caustic system for conditions other than reported. The operating lines tend to pinch the equilibrium curve, Figure No. 4, and the exact location of the equilibrium curve is uncertain. Depending on the individual interpretation of the data, a 50% difference in the number of transfer stages may be obtained. However, the location of the curve, while it changes the numerical values, does not change the observed dependence of the numbers of the operating variables.

One of the surprising features of the RDC column performance is the absence of solids build-up within the stirred zones. The machine might be capable of handling slurries. In general, the Rotating Disc Contactor develops a high transfer rate per unit volume, and is insensitive to small upsets in the feed system, and can tolerate significant quantities of solids within the column proper.

(8) Davies, J. T., Mayers, G. R. A., Chem. Engr. Sci. 16, 55 (1961).
(9) Gurney, C. F., Phys. Rev. 26, 98 (1908).

RDC EXTRACTION COLUMN PERFORMANCE
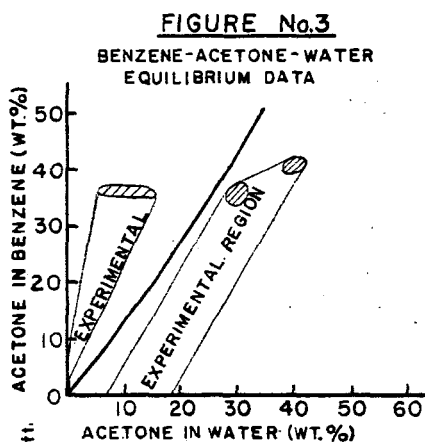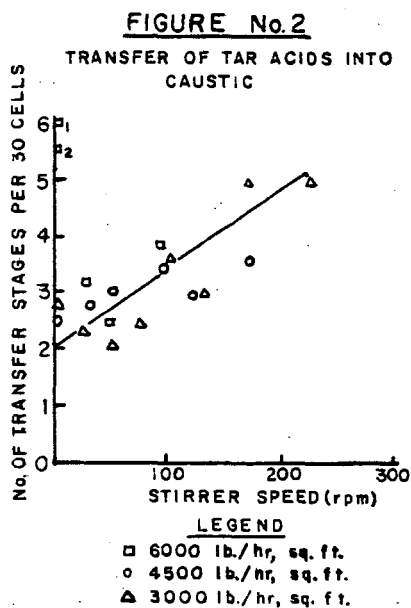## 24-36 CELLS 4 in I.D. 2 in.H. STIRRER DISC 2¼ in.D

FIGURE No.1
TRANSFER OF ACETONE BETWEEN BENZENE AND WATER

Y-axis: No. OF TRANSFER STAGES PER 30 CELLS
X-axis: STIRRER SPEED (rpm)

LEGEND
- ACETONE FROM WATER (24 CELLS)
- △ ACETONE FROM BENZENE (24 CELLS)
- ○ ACETONE FROM WATER (36 CELLS)

FIGURE No.2
TRANSFER OF TAR ACIDS INTO CAUSTIC

Y-axis: No. OF TRANSFER STAGES PER 30 CELLS
X-axis: STIRRER SPEED (rpm)

LEGEND
- 6000 lb./hr, sq. ft.
- ○ 4500 lb./hr, sq. ft.
- △ 3000 lb./hr, sq. ft.

FIGURE No.3
BENZENE-ACETONE-WATER EQUILIBRIUM DATA

Y-axis: ACETONE IN BENZENE (WT.%)
X-axis: ACETONE IN WATER (WT.%)
EXPERIMENTAL
EXPERIMENTAL REGION

FIGURE No.4
NEUTRAL OIL-TAR ACIDS- 9wt. % CAUSTIC SOLUTION EQUILIBRIUM DATA

Y-axis: TAR ACIDS IN CAUSTIC (wt. %)
X-axis: TAR ACIDS IN NEUTRAL OIL (wt %)
EXPERIMENTAL REGION

LEGEND
- TAR ACIDS DISPERSED PHASE
- △ BENZENE DISPERSED PHASE
- ○ WATER DISPERSED PHASE

FIGURE No.5
FLOODING LIMITS

Y-axis: TOTAL THROUGHPUT 1000 lb/hr, sq.ft.
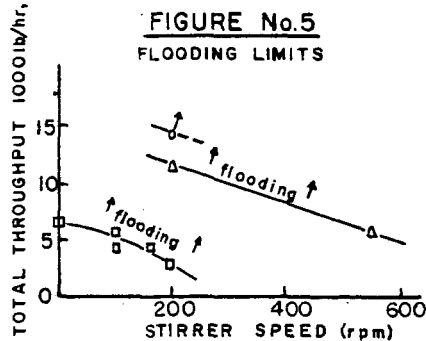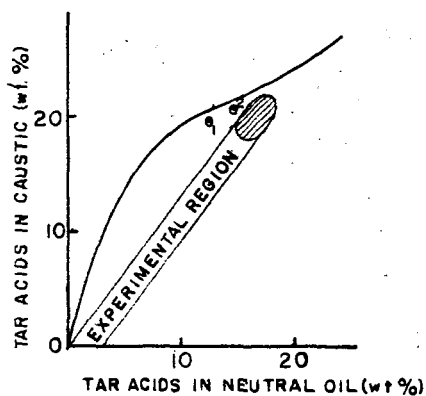X-axis: STIRRER SPEED (rpm)
flooding
flooding

TABLE I

Extraction of Tar Acids with 9 wt.% NaOH in Water. Feed to Solvent ratio 1.9 to 2.1. Tar Acid Oil dispersed phase.

Column Temperature °C	Rotor Speed rpm	Total Throughput lb./hr.,sq.ft.	Tar Feed wt.%	Acid Content Extract wt.%	NaOH in Solvent wt.%	No. of Transfer Stages
86	0	4700	14.9*	19.4	9.7	2.0
87	25	4100	14.9*	20.7	9.7	2.3
87	50	5000	14.9*	21.0	9.7	2.5
85	75	4100	14.9*	21.0	9.7	2.8
86	123	4100	16.8	20.2	9.2	2.5
88	165	4400	16.8	21.8	9.2	3.0
92	0	6800	12.5*	20.5	9.2	5.0
88	0	5800	14.3*	22.0	9.2	4.5
85	25	6300	16.8	23.0	9.8	2.7
85	50	6000	15.4	22.5	9.9	2.1
85	76	5800	17.4	23.5	9.6	3.2
86	0	3200	15.9	19.9	8.9	2.2
86	25	3400	15.9	19.5	8.8	2.1
84	50	3200	16.5	19.8	9.4	1.7
85	75	3300	16.5	21.0	9.2	2.1
85	100	3200	16.5	20.9	9.1	2.9
87	125	3100	16.5	20.3	9.1	2.5
85	171	3200	16.5	20.9	9.2	4.0
85	230	3100	16.5	22.2	9.5	4.0

*Synthetic of Wilton Still Tar Acid Oil and recovered Tar Acid from plant.

TABLE II

Transfer of Acetone between Benzene and Water at 23°C

Continuous Phase	Rotor Speed	Phase Throughput		Acetone Content			Transfer Stages
		Benzene	Water-Acetone	Feed Water-Acetone	Extract Benzene-Acetone	Raffinate Water-Acetone	
	rpm	lb./hr.,sq.ft.		Wt.%	Wt.%	Wt.%	No.
Benzene (24 cells)	100	350	650	40.5	41.9	15.1	2
	180	350	650	41.3	40.9	19.5	1.5
	375	350	650	39.6	41.8	11.5	3
	500	350	650	40.3	40.3	10.3	2.6
	500	700	1300	41.1	40.5	10.0	2.9
		Benzene-Acetone	Water	Benzene-Acetone	Water-Acetone	Benzene-Acetone	
Water (24 cells)	500	470	3000	37.8	4.2	0.1	2.8
	500	870	3000	36.5	9.5	1.3	2
	500	1430	3000	36.5	12	2.7	2.5
	500	1900	3000	36.5	15	2.7	3
		Benzene	Water-Acetone	Water-Acetone	Benzene-Acetone	Water-Acetone	
Water-Acetone (36 cells)	50	1400	3500	30.0	33	12.3	2.1
	145	1350	3300	30.0	33.7	12.5	2.5
	245	1450	3400	31.0	33.0	13.5	2.0
	320	1300	3700	29.0	35.0	10.7	3.5
	245	1450	3400	31.0	35.0	12.0	2.8
	305	1400	3750	30.0	36.5	12.0	3.2
	390	1400	3500	29.0	34.5	10.0	3.5
	500	1400	3750	29.0	34.5	8.4	3.7